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The reactions of tris(trimethylsilyl)silyllithium with ketenes[☆]

Akinobu Naka [a], Joji Ohshita [b], Atsutaka Kunai [b], Myong Euy Lee [c], Mitsuo Ishikawa [a,*]

[a] *Department of Chemical Technology, Kurashiki University of Science and the Arts, 2640 Nishinoura, Tsurajima-cho, Kurashiki, Okayama 712-8505, Japan*

[b] *Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan*

[c] *Department of Chemistry, Yonsei University, Wonju Campus, Wonju, Kangwondo 220-710, South Korea*

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Abstract

The reaction of diphenylketene with tris(trimethylsilyl)silyllithium, followed by hydrolysis of the mixture afforded 2,2-diphenyl-1-trimethylsiloxy-1-[bis(trimethylsilyl)silyl]ethene (**1**) in 78% yield. Treatment of the silyllithium adduct with chlorotrimethylsilane produced 2,2-diphenyl-1-trimethylsiloxy-1-[tris(trimethylsilyl)silyl]ethene (**2**) in 74% yield. A similar reaction of diphenylketene with the silyllithium in the presence of 2,3-dimethylbutadiene or isobutene, followed by treatment with chlorotrimethylsilane gave **2** as the sole product. The reaction of methylphenylketene with tris(trimethylsilyl)silyllithium, followed by hydrolysis of the resulting adduct, produced (E)-2-methyl-2-phenyl-1-trimethylsiloxy-1-bis(trimethylsilyl)silylethene in 76% yield, while with di(*tert*-butyl)ketene, the silyllithium afforded no adduct, but the starting ketene was recovered unchanged. Similar reaction of bis(trimethylsilyl)ketene with the silyllithium gave tetrakis(trimethylsilyl)silane in 54% yield. The X-ray crystallographic study for compound **2** is described. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ketenes; Tris(trimethylsilyl)silyllithium; Tris(trimethylsilyl)silyl adducts

1. Introduction

The Peterson reaction has been shown to be an useful route to the synthesis of olefins. The reaction involves addition of an α-silylcarbanion to the carbonyl group of aldehydes and ketones to give β-silyl alkoxides, which undergo elimination of silanolates to produce olefins [1,2]. We have demonstrated that treatment of acylpolysilanes with organolithium reagents affords silenes, via a Peterson-type reaction. The reaction involves addition of the organolithium compounds to a carbonyl group in the acylpolysilanes, followed by elimination of lithium silanolates to give silenes [3]. Brook et al. [4], Apeloig et al. [5], and Oehme et al. [6] have found that the silenes can be obtained by the Peterson-type reactions of the other silicon system. On the other hand, it has been reported that alkyl- and aryllithium reagents react with ketenes to give adducts [7–13]. In these reactions the lithium reagents add to the carbonyl group of ketenes giving lithium enolates.

We also found that the reaction of the acyl-tris(trimethylsilyl)silanes with tris(trimethylsilyl)silyllithium affords no products originated from addition of a silyl anion to a carbonyl group, but produces lithium silenolates, in which the silyl anion abstracts a trimethylsilyl group from the tris(trimethylsilyl)silyl moiety in acylpolysilanes [14]. As a part of our study concerning the reaction of the silyl anion with carbonyl compounds, we investigated the reactions of tris(trimethylsilyl)silyllithium with ketenes, and found that the tris(trimethylsilyl)silyl adducts thus formed undergo a 1,3-trimethylsilyl shift from the silyl center to an oxy anion giving silyl anions, but not the Peterson-type elimination.

[☆] This paper is dedicated to the memory of the late Professor Rokuro Okawara.

[*] Corresponding author.

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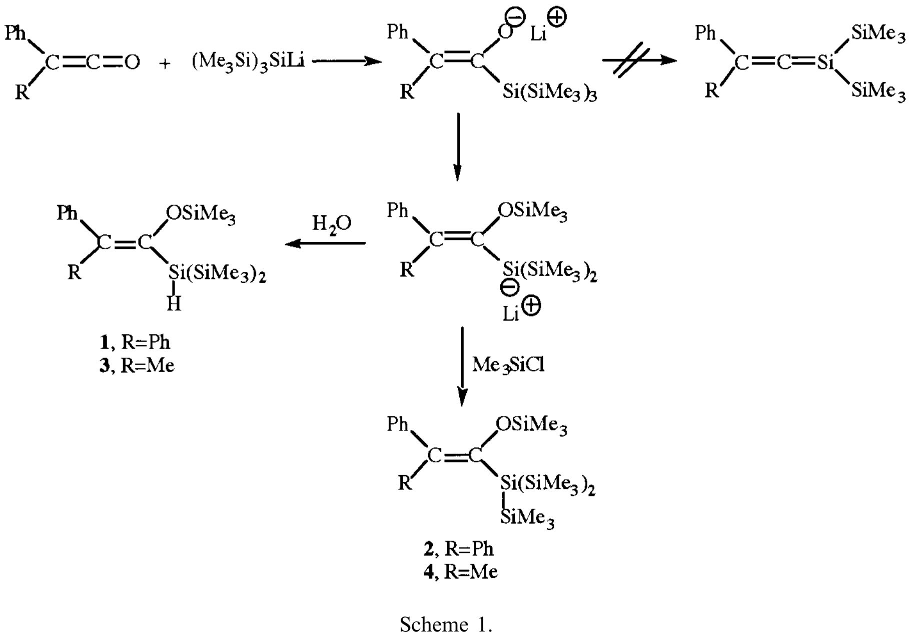
2. Results and discussion

2.1. The reactions of tris(trimethylsilyl)silyllithium with ketenes

When diphenylketene was treated with one equivalent of tris(trimethylsilyl)silyllithium at −90°C for 30 min and the resulting mixture was hydrolyzed with water, a product identified as 2,2-diphenyl-l-trimethylsiloxy-1-[bis(trimethylsilyl)silyl]ethene (**1**) was obtained in 78% yield (Scheme 1). No other volatile products were detected by either spectrometric analysis or GLC analysis of the reaction mixture. The ^{1}H-NMR spectrum of **1** shows three signals at δ −0.09, 0.16 and 3.18 ppm due to two non-equivalent trimethylsilyl protons and an Si–H proton, as well as signals at 7.12–7.25 ppm assigned to phenyl ring protons. The ^{13}C-NMR spectrum reveals two resonances of trimethylsilyl carbons at 0.6 and 1.0 ppm and two olefinic carbons at 143.1 and 152.1 ppm, as well as eight resonances of phenyl ring carbons. The ^{29}Si-NMR spectrum shows three resonances at −62.6, −13.7, and 16.4 ppm, respectively. These results are wholly consistent with the structure proposed for product **1**.

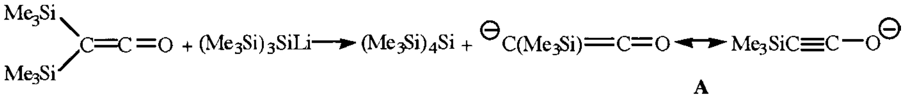
In order to clarify the structure of the anionic species formed in this reaction, we quenched the reaction mixture with chlorotrimethylsilane. To our surprise, 2,2-diphenyl-1-trimethylsiloxy-1-[tris(trimethylsilyl)-silyl]-ethene (**2**) was obtained in 74% yield, as the sole product, indicating that the anion is present on the bis(trimethylsilyl)substituted silicon atom, but not on the oxygen atom. The structure of **2** was verified by spectrometric analysis and also by X-ray crystallographic study as shown below. We previously reported that the reaction of benzoyltris(trimethylsilyl)silane with aryllithium, followed by hydrolysis of the resulting mixture gave [aryl(phenyl)methyl](trimethylsiloxy)bis-(trimethylsilyl)silane, which was produced from addition of lithium trimethylsiloxide to 2-aryl-2-phenyl-1,1-bis(trimethylsilyl)silene, arising from a Peterson-type reaction of the aryllithium-acylpolysilane adduct [3b]. Product **1** and **2** might be considered to be produced by elimination and addition of the ketene-silyllithium adduct as observed in the reaction of the acylpolysilane with aryllithium. In order to check this possibility, we carried out the reaction in the presence of a trapping agent. Thus, the reaction of diphenylketene with tris(trimethylsilyl)silyllithium in the presence of 2,3-dimethylbutadiene, followed by treatment of the resulting mixture with chlorotrimethylsilane, again afforded product **2** in 64% yield. In the presence of isobutene, the reaction of diphenylketene with tris(trimethylsilyl)silyllithium again produced **2** in 62% yield, after treatment of the mixture with chlorotrimethylsilane. No adducts arising from the reaction of a silene which might be formed by addition of the silyllithium to a carbonyl group of diphenylketene, followed by Peterson-type elimination with the trapping agents were detected at all. Therefore, the formation of **1** and **2** may be best understood in terms of a 1,3-trimethylsilyl shift from silicon center onto an oxygen anion. An intramolecular 1,3-silyl shift to the oxygen atom is probably more favorable than the Peterson-type elimination of the lithium trimethylsilyloxide in the silyllithium-ketene adduct. The 1,3-shift of a trimethylsilyl group on the silicon atom onto an oxy anion has been observed in the reaction of tris(trimethylsilyl)silylmethanol with sodium–potassium alloy by Brook and Crusciel [15].



1, R=Ph
3, R=Me

2, R=Ph
4, R=Me

Scheme 1.



Scheme 2.

Wustrack and Oehme also found a similar 1,3-silyl shift in the reaction of aliphatic ketones with tris(trimethylsilyl)silyllithium [16].

Treatment of methylphenylketene with tris(trimethylsilyl)silyllithium under the same conditions, and then hydrolysis of the resulting mixture gave (E)-2-methyl-2-phenyl-1-trimethylsiloxy-1-bis(trimethylsilyl)silylethene (**3**) in 67% yield. Similar reaction of methylphenylketene with the silyllithium, followed by treatment with chlorotrimethylsilane afforded (E)-2-methyl-2-phenyl-1-trimethylsiloxy-1-tris(trimethylsilyl)silylethene (**4**) in 69% yield. Again the formation of products **3** and **4** may be explained in terms of a 1,3-trimethylsilyl shift in the anionic species. The stereospecific formation of E-olefins **3** and **4** seems to be due to steric hindrance. The silyl anion probably adds to a carbonyl group from a less hindered site. In fact, it has been found that the reactions of methylphenylketene, ethylphenylketene, and ethyl(trimethylsilyl)ketene with *n*-butyllithium proceed with the same fashion as that of the present reaction to give the adducts with high stereospecificity [13].

Next, we attempted the similar reaction with a ketene bearing bulky substituents. Thus, treatment of di(*tert*-butyl)ketene with tris(trimethylsilyl)silyllithium in THF under the same conditions as above afforded no adduct, but the starting ketene was recovered unchanged. Presumably, the silyl anion could not add a carbonyl group of this ketene, because of steric hindrance. In this reaction, tris(trimethylsilyl)silane produced from hydrolysis of the starting silyllithium was obtained in 89% yield.

The reaction of bis(trimethylsilyl)ketene with the silyllithium reagent proceeded with a different fashion from that of diphenyl- and methylphenylketene. In this reaction, tetrakis(trimethylsilyl)silane was obtained in 56% yield, together with small amounts of many products (less than 3% yield). Presumably, the tris(trimethylsilyl)silyl anion abstracts a trimethylsilyl group from the silylketene to give tetrakis(trimethylsilyl)silane and the anion **A**, which decomposes to give non-volatile products under the conditions used (Scheme 2). In order to trap the anion, we treated bis(trimethylsilyl)ketene with tris(trimethylsilyl)silyl anion at −90°C and warmed up to 0°C, then added *tert*-butyldimethylchlorosilane to the mixture. Again, tetrakis(trimethylsilyl)silane was obtained in 60% yield, in addition to many products in less than 3% yields. GC-Mass spectrometric analysis of the reaction mixture showed that the product having a molecular weight of m/z 228, corresponding to (t-BuMe$_2$Si)(Me$_3$Si)C=C=O was produced in 3% yield. Unfortunately, all attempts to isolate this compound were unsuccessful. In fact, it has been reported that the reaction of trimethylsilylketene with *n*-butyllithium at −78°C, followed by quenching the solution with trimethylchlorosilane gives bis(trimethylsilyl)ketene in 23% yield, while at −100°C, the same reaction affords bis(trimethylsilyl)ketene in excellent yield [17]. In the present reaction, however, abstraction of a trimethylsilyl group of bis(trimethylsilyl)ketene by tris(trimethylsilyl)silyllithium occurs at temperature near 0°C, but not at low temperature, although a lithium–trimethylsilyl exchange in the reaction of acyltris(trimethylsilyl)silane with silyllithium reagents has been observed to occur at low temperature. The anion produced at 0°C would mainly decompose to give non-volatile substances.

2.2. *X-ray crystallographic analysis for **2***

Only a few papers concerning X-ray crystallographic study for silyl enol ethers have been reported so far [18–23]. The structure of **2** was determined by a single crystal X-ray diffraction study. Cell dimensions, data collections and refinement parameters, atomic coordinates, and selected bond lengths, angles and torsion angles for **2** are summarized in Tables 1–3. An ORTEP view of **2** is presented in Fig. 1, along with an atom-numbering scheme.

As shown in Fig. 1, the crystal structure of **2** consists of a silyl enol ether fragment bearing a highly crowded silyl substituent. Two phenyl groups are located on the C2 atom with twisted angles of 37.9(3) and 51.0(4)°, respectively, from the plane involving C1, C2, C3, C9. It is likely that these two phenyl groups and a tris(trimethylsilyl)silyl substituent provide the steric shielding of the enol unit leading to resistance of compound **2** toward hydrolysis.

Appreciable deviation of the bond angle of Si1–C1–C2 = 129.1(2)° from ideal sp^2 hybridization seems to be due to the steric repulsion between the tris(trimethylsilyl)silyl and phenyl group. The enol C1=C2 bond is twisted as demonstrated by torsion angles of Si1–C1–C2–C3 = −30.6(4)° and O1–C1–C2–C9 = −14.7(3)°, again reflecting the highly crowded structure around the enol unit, although enol sp^2 carbons almost retain their planarity (sum of angles at C1, 359.0°; C2, 360.0°). The C1=C2 bond length was determined to be

1.355(3) Å, longer than the values reported so far for silyl enol ethers with a nearly or complete planar structure (1.304–1.337Å [18–22]), in accordance with the twisted form of compound **2**. Some $n(\mathrm{O})-\pi(\mathrm{C{=}C})$ interaction in the enol unit might be an alternative explanation for the longer bond length in the C1=C2 bond. The torsion angle of C2–C1–O1–Si5 = −66.3(3)°, however, suggests the absence of such interaction in compound **2**. Similar elongation in the enol C=C bond has been recently reported for a highly crowded silyl enol ether, $\mathrm{Mes_2C{=}CPh[OSiMe_2(\textit{p}\text{-anisyl})]}$ (C=C = 1.345(3) Å), which has a twisted enol unit with torsion angles of Mes–C=C–Ph = 12.6(3)° and MesC=C–O = 7.1(3)° [23].

3. Experimental section

3.1. General procedure

Yields of the products were determined by analytical GLC with the use of tridecane as an internal standard, on the basis of the starting compounds used. NMR spectra were recorded on a JEOL Model JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND20 infrared spectrometer. Low-resolution mass spectra and High-resolution mass spectra were measured on a JEOL Model JMS-700 instrument.

Table 1
Crystal data, experimental conditions, and summary of structural refinement for compound **2**

Molecular formula	$C_{26}H_{46}Si_5O$
Molecular weight	515.08
Space group	$P\bar{1}$
Cell dimensions	
a (Å)	9.742(5)
b (Å)	18.541(5)
c (Å)	9.596(3)
α (°)	95.22(3)
β (°)	106.44(3)
γ (°)	100.38(3)
V (Å^3)	1616(1)
Z	2
D_{calc} (mg m^{-3})	1.058
F_{000}	560.00
Crystal size (mm^3)	0.5 × 0.4 × 0.4
Crystal color	Colorless
μ (mm^{-1})	2.36
Diffractometer	Rigaku AFC-7R
Temperature (K)	298
Wavelength (Å)	0.71069 (Mo–K$_\alpha$)
Monochrometer	Graphite crystal
Scan type	ω–2θ
Scan speed (° min^{-1})	16
Scan width (°)	$0<2\theta<55.0$
No. of unique reflections	7415
No. of observed reflections ($\lvert F_o\rvert \geq 3\sigma(F_o)$)	5196
R	0.043
R_w*	0.044

* Weighting scheme is $(\sigma(F_o)^2+0.0004\,|\,F_o\,|\,2)^{-1}$.

Table 2
Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **2** with estimated S.D. in parentheses

Atom	*x*	*y*	*z*	B_{eq} [a]
Si1	0.58746(7)	0.28157(4)	0.81145(7)	3.04(1)
Si2	0.64906(8)	0.39954(4)	0.73989(9)	3.97(2)
Si3	0.58727(9)	0.29425(5)	1.05895(8)	4.11(2)
Si4	0.78609(9)	0.22464(5)	0.80203(9)	4.36(2)
Si5	0.31082(9)	0.07269(4)	0.68970(9)	4.31(2)
O1	0.4329(2)	0.14302(9)	0.6665(2)	3.68(4)
C1	0.4207(3)	0.2169(1)	0.6682(2)	3.02(5)
C2	0.3139(3)	0.2342(1)	0.5600(3)	3.16(5)
C3	0.2638(3)	0.3049(1)	0.5724(3)	3.62(5)
C4	0.2204(4)	0.3407(2)	0.4510(4)	5.37(8)
C5	0.1610(4)	0.4035(2)	0.4633(5)	7.1(1)
C6	0.1438(4)	0.4298(2)	0.5933(6)	7.3(1)
C7	0.1844(4)	0.3950(2)	0.7132(5)	6.18(9)
C8	0.2431(3)	0.3326(2)	0.7022(3)	4.53(7)
C9	0.2331(3)	0.1814(1)	0.4222(3)	3.65(5)
C10	0.0803(3)	0.1678(2)	0.3651(3)	4.84(7)
C11	0.0084(4)	0.1219(2)	0.2329(4)	6.59(9)
C12	0.0854(6)	0.0903(2)	0.1552(4)	7.5(1)
C13	0.2364(5)	0.1033(2)	0.2088(4)	7.1(1)
C14	0.3095(4)	0.1487(2)	0.3421(3)	5.14(8)
C15	0.1627(5)	0.1076(2)	0.7415(5)	8.2(1)
C16	0.2356(6)	0.0033(2)	0.5244(5)	9.7(1)
C17	0.4045(5)	0.0287(3)	0.8414(6)	11.1(2)
C18	0.6141(4)	0.3894(2)	0.5364(4)	6.7(1)
C19	0.5598(4)	0.4728(2)	0.7973(5)	6.9(1)
C20	0.8510(3)	0.4374(2)	0.8273(4)	6.06(9)
C21	0.7301(5)	0.3790(2)	1.1608(4)	7.9(1)
C22	0.6372(5)	0.2141(2)	1.1494(4)	7.8(1)
C23	0.4097(4)	0.3062(2)	1.0851(4)	6.8(1)
C24	0.9594(3)	0.2721(2)	0.9517(4)	6.54(9)
C25	0.7588(4)	0.1248(2)	0.8263(4)	5.81(9)
C26	0.8170(4)	0.2296(2)	0.6193(4)	7.1(1)

[a] $B_{\mathrm{eq}}=(4/3)(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\beta)$.

3.2. Reaction of tris(trimethylsilyl)silyllithium with diphenylketene

In a 30 ml two-necked flask equipped with a stirrer was placed a solution of 0.1357 g (0.699 mmol) of diphenylketene in 5 ml THF. To this was added a solution of tris(trimethylsilyl)silyllithium prepared by the reaction of 0.2356 g (0.736 mmol) of tetrakis(trimethylsilyl)silane with 0.810 mmol of a methyllithium–ether solution in 5 ml of THF at −90°C by the use of syringe. The mixture was stirred at −90°C for 30 min, and allowed to stand at room temperature for 3 h. After hydrolysis of the mixture with 0.05 ml of water, the solvent was evaporated, and the resulting mixture was analyzed by GLC as being **1** (78% yield). Compound **1** was isolated by column chromatography:

Table 3
Bond lengths (Å), angles (°), and selected torsion angles (°) for compound **2** with estimated S.D. in parentheses

Bond lengths					
Si1–Si2	2.377(1)	Si1–Si3	2.366(1)	Si1–Si4	2.384(1)
Si1–C1	1.924(2)	Si2–C18	1.870(4)	Si2–C19	1.862(4)
Si2–C20	1.878(3)	Si3–C21	1.877(4)	Si3–C22	1.859(4)
Si3–C23	1.865(4)	Si4–C24	1.885(4)	Si4–C25	1.868(4)
Si4–C26	1.868(4)	Si5–O1	1.676(2)	Si5–C15	1.852(4)
Si5–C16	1.827(4)	Si5–C17	1.829(4)	O1–C1	1.394(3)
C1–C2	1.355(3)	C2–C3	1.485(3)	C2–C9	1.492(3)
C3–C4	1.392(4)	C3–C8	1.386(4)	C4–C5	1.400(5)
C5–C6	1.363(6)	C6–C7	1.366(6)	C7–C8	1.387(4)
C9–C10	1.399(4)	C9–C14	1.384(4)	C10–C11	1.382(4)
C11–C12	1.363(6)	C12–C13	1.382(6)	C13–C14	1.386(4)
Bond angles					
Si2–Si1–Si3	110.88(4)	Si2–Si1–Si4	104.20(4)	Si2–Si1–C1	112.77(8)
Si3–Si1–Si4	106.69(4)	Si3–Si1–C1	117.39(8)	Si4–Si1–C1	103.55(8)
Si1–Si2–C18	110.0(1)	Si1–Si2–C19	116.6(1)	Si1–Si2–C20	108.4(1)
C18–Si2–C19	109.4(2)	C18–Si2–C20	106.9(2)	C19–Si2–C20	105.0(2)
Si1–Si3–C21	107.5(1)	Si1–Si3–C22	112.2(1)	Si1–Si3–C23	114.6(1)
C21–Si3–C22	107.4(2)	C21–Si3–C23	107.5(2)	C22–Si3–C23	107.3(2)
Si1–Si4–C24	111.2(1)	Si1–Si4–C25	115.0(1)	Si1–Si4–C26	109.3(1)
C24–Si4–C25	105.2(2)	C24–Si4–C26	109.2(2)	C25–Si4–C26	106.7(2)
O1–Si5–C15	110.5(1)	O1–Si5–C16	111.0(2)	O1–Si5–C17	108.3(2)
C15–Si5–C16	110.9(2)	C15–Si5–C17	107.5(2)	C16–Si5–C17	108.5(3)
Si5–O1–C1	126.4(2)	Si1–C1–O1	111.1 (2)	Si1–C1—C2	129.1(2)
O1–C1–C2	118.8(2)	C1–C2–C3	122.9(2)	C1–C2–C9	121.8(2)
C3–C2–C9	110.3(2)	C2–C3–C4	121.5(3)	C2–C3–C8	120.3(2)
C4–C3–C8	117.8(3)	C3–C4–C5	120.1(3)	C4–C5–C6	120.5(3)
C5–C6–C7	120.2(3)	C6–C7–C8	119.8(4)	C3–C8–C7	121.6(3)
C2–C9–C10	121.4(2)	C2–C9–C14	120.1(2)	C10–C9–C14	118.3(3)
C9–C10–C11	120.4(3)	C10–C11–C12	120.0(3)	C11–C12–C13	120.2(3)
C12–C13–C14	119.8(4)				
Torsion angles					
Si1–C1–C2–C3	$-30.6(4)$	O1–C1–C2–C9	$-14.7(3)$	C2–C1–O1–Si5	$-66.3(3)$

m.p. 92–93°C; MS m/z 442(M^+); IR 3077, 2954, 2923, 2098, 1596, 1490, 1442, 1247, 1186, 1122, 956, 862, 836, 754, 701, 657, 617, 603 cm^{-1}; ^{1}H-NMR δ($CDCl_3$) -0.09 (s, 9H, Me_3Si), 0.16 (s, 18H, Me_3Si), 3.18 (s, 1H, HSi), 7.12–7.25 (m, 10H, phenyl ring protons); ^{13}C-NMR δ($CDCl_3$) 0.6, 1.0 (Me_3Si), 126.4, 127.0, 127.8, 128.0, 130.5, 130.7, 140.9, 141.6 (phenyl ring carbons) 143.1, 152.1 (olefinic carbons); ^{29}Si-NMR δ($CDCl_3$) -62.6, -13.7, 16.4. Anal. Calc. for $C_{23}H_{38}OSi_4$: C, 62.37; H, 8.65. Found: C, 62.37; H, 8.67.

*3.3. 2,2-Diphenyl-1-trimethylsiloxy-1-tris(trimethylsilyl)silylethene (**2**)*

In a 30 ml two-necked flask equipped with a stirrer was placed a solution of 0.1441 g (0.743 mmol) of diphenylketene in 5 ml THF. To this was added a solution of tris(trimethylsilyl)silyllithium prepared from 0.2464 g (0.770 mmol) of tetrakis(trimethylsilyl)silane and 0.847 mmol of methyllithium in 5 ml of THF at -90°C. The mixture was stirred at the same temperature and warmed up to room temperature, and then allowed to stand for 3 h. After 0.1250 g (1.15 mmol) of chlorotrimethylsilane was added by a syringe, the mix-

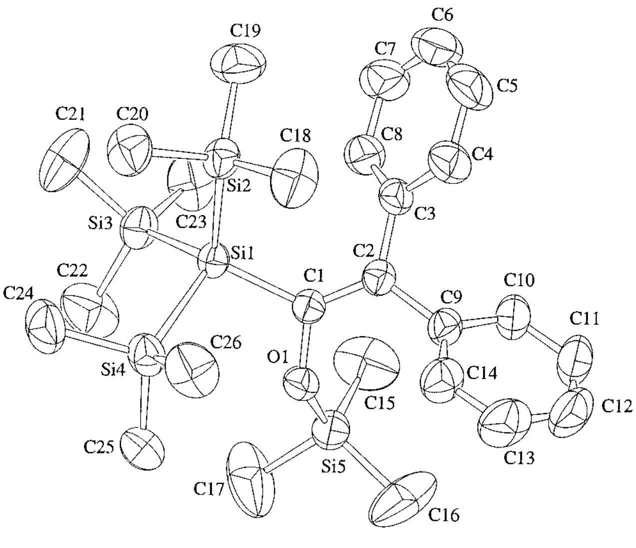


Fig. 1. Molecular structure of compound **2** with atomic numbering scheme.

ture was analyzed by GLC as being **2** (74% yield). Compound **2** was isolated by column chromatography: m.p. 132–133°C; MS *m/z* 514 (M^+); IR 2952, 2915, 2848, 1633, 1438, 1241, 1172, 1089, 1072, 948, 835, 763, 696, 624 cm^{-1}; ^{1}H-NMR δ($CDCl_3$) -0.18 (s, 9H, Me_3Si), 0.13 (s, 27H, Me_3Si), 7.06–7.24 (m, 10H, phenyl ring protons); ^{13}C-NMR δ($CDCl_3$) 1.7, 2.4 (Me_3Si), 126.6, 127.4, 128.0, 128.7, 132.17, 132.24, 142.8, 143.3 (phenyl ring carbons) 144.1, 155.0 (olefinic carbons); ^{29}Si-NMR δ($CDCl_3$) -70.2, -12.0, 17.0. Anal. Calc. for $C_{26}H_{46}OSi_5$: C, 60.63; H, 9.00. Found: C, 60.67; H, 9.27.

3.4. Reaction of diphenylketene with tris(trimethylsilyl)-silyllithium in the presence of 2,3-dimethylbutadiene

In a 30 ml two-necked flask was placed a mixture of 0.1501 g (0.774 mmol) of diphenylketene and 0.6235 (7.59 mmol) of 2,3-dimethylbutadiene in 5 ml of THF. To this was added a solution of tris(trimethylsilyl)silyllithium (from 0.2518 g (0.787 mmol) of tetrakis(trimethylsilyl)silane) in 5 ml of THF at -90°C. The mixture was stirred for 30 min at -90°C and then warmed up to room temperature. After 0.1281 g (1.18 mmol) of chlorotrimethylsilane was added to the mixture by syringe, the mixture was analyzed by GLC as being **2** (64% yield). Compound **2** was isolated by column chromatography. All spectral data for **2** were identical with those of an authentic sample obtained from the above reaction.

3.5. Reaction of diphenylketene with tris(trimethylsilyl)-silyllithium in the presence of isobutene

In a 30 ml two-necked flask was placed a mixture of 0.1618 g (0.834 mmol) of diphenylketene and 0.7105 g (12.7 mmol) of isobutene in 5 ml THF. To this was added a solution of tris(trimethylsilyl)silyllithium (from 0.2635 g (0.823 mmol) of tetrakis(trimethylsilyl)silane) in 5 ml of THF at -90°C. After the mixture was warmed up to room temperature, 0.1072 g (0.988 mmol) of chlorotrimethylsilane was added, and then analyzed by GLC as being **2** (62% yield). Compound **2** was isolated by column chromatography. All spectral data for **2** were identical with those of an authentic sample obtained from above reaction.

3.6. Reaction of methylphenylketene with tris-(trimethylsilyl)silyllithium

In a 30 ml two-necked flask was placed a solution of 0.2274 g (1.35 mmol) of methylphenylketene in 5 ml THF. To this was added 1.3 mmol of a tris(trimethylsilyl)silyllithium–THF solution at -90°C. The mixture was stirred for 30 min and warmed to room temperature. After hydrolysis of the mixture with 0.03 ml of water, the solvent was evaporated, and then analyzed by GLC as being **3** (67% yield). Compound **3** was isolated by column chromatography: MS *m/z* 380 (M^+); IR 3057, 2953, 2895, 2085, 1598, 1493, 1443, 1246, 1132, 876, 837, 781, 758, 696, 617 cm^{-1}; ^{1}H-NMR δ($CDCl_3$) -0.13 (s, 9H, Me_3Si), 0.27 (s, 18H, Me_3Si), 1.97 (s, 3H, Me), 3.45 (s, 1H, HSi), 7.15–7.34 (m, 5H, phenyl ring protons); ^{13}C-NMR δ($CDCl_3$) 0.6, 0.8 (Me_3Si), 21.8 (Me), 126.0, 127.7, 128.8, 131.4 (phenyl ring carbons) 141.7, 147.1 (olefinic carbons); ^{29}Si-NMR δ($CDCl_3$) -63.9, -13.8, 15.6. Exact mass calc. for $C_{18}H_{36}Si_4O$ (M^+) 380.1843, found 380.1858.

3.7. (E)-2-Methyl-2-phenyl-1-trimethylsilyl-oxy-1-tris(trimethylsilyl)silylethene (4)

In a 30 ml two-necked flask was placed 0.2557 g (1.52 mmol) of methylphenylketene in 5 ml THF. The mixture was stirred for 30 min at -90°C, and warmed up to room temperature. After 0.2475 g (2.28 mmol) of chlorotrimethylsilane was added, the mixture was analyzed by GLC as being **4** (69% yield). Compound **4** was isolated by column chromatography: MS *m/z* 452 (M^+); IR 3057, 2951, 2895, 1493, 1443, 1398, 1246, 1111, 835, 758, 698, 622 cm^{-1}; ^{1}H-NMR δ($CDCl_3$) -0.26 (s, 9H, Me_3Si), 0.29 (s, 27H, Me_3Si), 2.04 (s, 3H, Me), 7.28–7.30 (m, 5H, phenyl ring protons); ^{13}C-NMR δ($CDCl_3$) 1.5, 2.5 (Me_3Si), 25.0 (Me), 126.4, 128.2, 129.8, 132.8 (phenyl ring carbons) 143.3, 150.1 (olefinic carbons); ^{29}Si-NMR δ($CDCl_3$) -76.4, -11.7, 14.8. Exact mass calc. for $C_{21}H_{44}Si_5O$ (M^+) 452.2239, found 452.2226.

3.8. Reaction of di(tert-butyl)ketene with tris-(trimethylsilyl)silyllithium

In a 30 ml two-necked flask was placed a solution of 0.1630 g (1.06 mmol) of di(*tert*-butyl)ketene in 5 ml THF. To this was added 0.823 mmol of tris(trimethylsilyl)silyllithium in 5 ml of THF at -90°C. The mixture was stirred for 30 min at -90°C and warmed up to room temperature. The mixture was hydrolyzed with water. GLC analysis of the hydrolyzed product showed that the starting ketene was recovered unchanged and a 89% yield of tris(trimethylsilyl)silane was produced.

3.9. Reactions of bis(trimethylsilyl)ketene with tris-(trimethylsilyl)silyllithium

In a 30 ml two-necked flask was placed a solution of 0.1378 g (0.741 mmol) of bis(trimethylsilyl)-ketene in 5 ml THF. To this was added 0.802 mmol of tris(trimethylsilyl)silyllithium at −90°C. The mixture was stirred for 30 min and warmed up to room temperature slowly, and hydrolyzed with water. The resulting mixture was analyzed by GLC as being 56% of tetrakis(trimethylsilyl)silane and many volatile products in less than 3% yields. Tetrakis(trimethylsilyl)silane was isolated by column chromatography. All spectral data for tetrakis(trimethylsilyl)silane was identical with those of an authentic sample.

3.10. Reaction of bis(trimethylsilyl)ketene with tris-(trimethylsilyl)silyllithium and treatment with tert-butyldimethylchlorosilane

To a solution of 0.1013 g (0.545 mmol) of bis(trimethylsilyl)ketene in 5 ml THF was added dropwise 0.620 mmol of a tris(trimethylsilyl)silyllithium–THF solution. The mixture was stirred for 30 min and then warmed up to 0°C. *tert*-Butyldimethylchlorosilane (0.1232 g, 0.819 mmol) was added to the mixture by a syringe and analyzed by GLC as being 60% of tetrakis(trimethylsilyl)silane, and 3% of a product (m/z 228), and many volatile products in less than 3% yields. Tetrakis(trimethylsilyl)silane was isolated by column chromatography. All spectral data for tetrakis(trimethylsilyl)silane was identical with those of an authentic sample.

*3.11. X-ray crystallographic analysis of compound **2***

All unique diffraction maxima with $0 < 2\theta < 55°$ were recorded on a Rigaku AFC-7R automated four-circle diffractometer using graphite-monochromated Mo–K_α radiation. Scans were carried out at a rate of 16° min^{-1} and weak reflections with $I < 10\sigma(I)$ were rescanned up to five times and the counts were accumulated. Refractions with $I > 3\sigma(I)$ were used in the least-squares refinement. The structure was solved by the SIR92 direct method [24] and expanded using DIRDIF94 Fourier techniques [25]. The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber [26]. Anomalous dispersion effects were included in F_{calc} [27]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [28]. The values for the mass attenuation coefficients are those of Creagh and Hubbel [29]. All calculations were performed using the teXsan [30] crystallographic software package of Molecular Structure Corporation.

4. Supplementary material available

Tables of anisotropic thermal parameters and observed and calculated structure factors for **2** may be obtained from N.A. on request.

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